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WATER QUALITY
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MISCELLANEOUS PAPER EL-90-14

PROCEEDINGS OF THE SIXTH
CORPS CHEMISTS MEETING
16-17 MAY 1989

compiled by

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Environmental Laboratory

DEPARTMENT OF THE ARMY

Waterways Experiment Station, Corps of Engineers
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September 1990

Final Report

Approved for Public Release Distribution Unlimited

Prepared for DEPARTMENT OF THE ARMY
US Army Corps of Engineers
Washington, DC 20314-1000

Under Water Quality Work Unit 31766

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SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited.		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Miscellaneous Paper EL-90-14			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION USAEWES Environmental Laboratory		6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION		
6c. ADDRESS (City, State, and ZIP Code) 3909 Halls Ferry Road Vicksburg, MS 39180-6199			7b. ADDRESS (City, State, and ZIP Code)		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION US Army Corps of Engineers		8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER Water Quality Work Unit 31766, "Analytical Procedures for Water and Wastewater"		
8c. ADDRESS (City, State, and ZIP Code) Washington, DC 20314-1000			10. SOURCE OF FUNDING NUMBERS		
PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO. 31766		
11. TITLE (Include Security Classification) Proceedings of the Sixth Corps Chemists Meeting, 16-17 May 1989					
12. PERSONAL AUTHOR(S)					
13a. TYPE OF REPORT Final report		13b. TIME COVERED FROM _____ TO _____		14. DATE OF REPORT (Year, Month, Day) September 1990	
15. PAGE COUNT 42					
16. SUPPLEMENTARY NOTATION Available from National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161.					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) See reverse.		
FIELD	GROUP	SUB-GROUP			
19. ABSTRACT (Continue on reverse if necessary and identify by block number) This paper contains a summary of the Proceedings of the Sixth Corps Chemists Meeting. Presentations and discussions centered around analytical methods used by the Corps, the expanding Corps mission in HTW work, the continuing importance of water quality programs, quality assurance for Corps projects, and communications between field and laboratory personnel.					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL			22b. TELEPHONE (Include Area Code)		22c. OFFICE SYMBOL

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE

18. SUBJECT TERMS (Continued).

Metals,

Petroleum hydrocarbons,

Polychlorinated biphenyls (PCBs) ,

Quality assurance ,

TNT,

Underground storage tanks .

Water quality . . .

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE

Preface

This paper summarizes the Proceedings of the Sixth Corps Chemists Meeting held 16-17 May 1989 at the US Army Engineer Waterways Experiment Station (WES), Vicksburg, MS. The Analytical Laboratory Group (ALG), Environmental Engineering Division (EED), Environmental Laboratory (EL), was the host and coordinated this activity as part of Water Quality Work Unit 31766, "Analytical Procedures for Water and Wastewater," which is sponsored by Headquarters, US Army Corps of Engineers (HQUSACE). The Water Quality work unit is managed within EL's Environmental Resources Research and Assistance Programs, Mr. J. Lewis Decell, Manager. The Technical Monitor for HQUSACE is Mr. Dave Buelow. Ms. Lynn Lamar, HQUSACE, assisted in the coordination of this meeting.

This report was compiled by Ms. Ann B. Strong and Ms. Agnes Morrow of the ALG, EL, and was edited by the Information Technology Laboratory. This report was prepared under the general supervision of Dr. Raymond L. Montgomery, Chief, EED, and Dr. John Harrison, Chief, EL.

COL Larry B. Fulton, EN, was the Commander and Director of WES and Dr. Robert W. Whalin was the Technical Director.

This report should be cited as follows:

Strong, Ann B., and Morrow, Agnes B. 1990. "Proceedings of the Sixth Corps Chemists Meeting, 16-17 May 1989," Miscellaneous Paper EL-90-14, US Army Engineer Waterways Experiment Station, Vicksburg, MS.

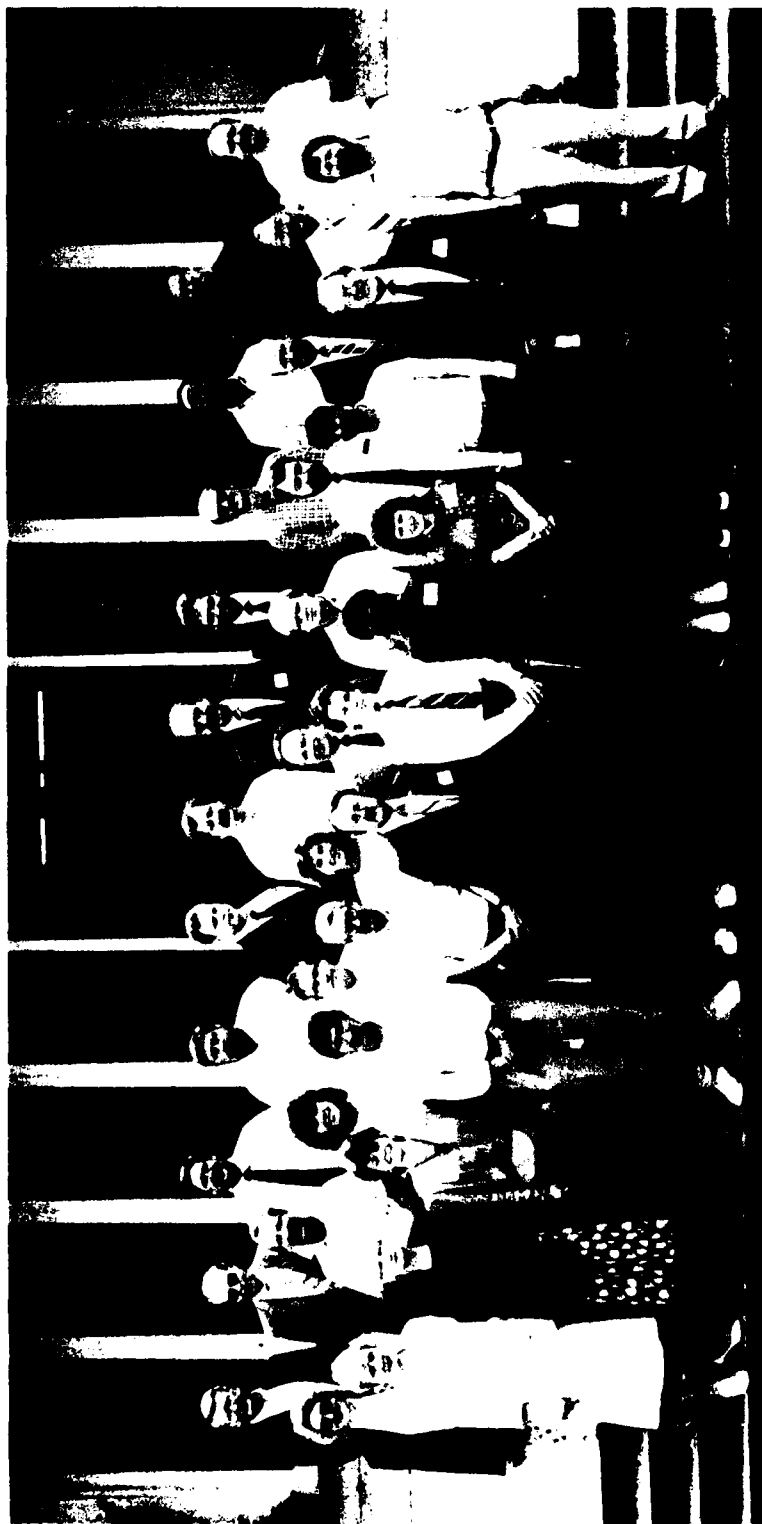
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CORPS CHEMISTS MEETING - 1989

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Row 2. Ann Strong, WES; John Schott, St. Louis District; Tracey Hooper, Nashville District; Newberry Brown, WES; Lynn Lamar, OCE; Marty Stutz, USATHAMA; Dave Bowman, Detroit District; Charles Reynolds, CRREL; Doug Taggart, MRD; Chung Rae Mao, MRD; Jerry Montgomery, Kansas City District.

Row 3. Jim Paxton, NPD Lab; Richard Kissinger, MRD Lab; Lance Hines, Omaha District; Doug Webb, Nashville District; Jim Nowland, SAD Lab; Dave Koran, ORD; Bruce Heitke, OCE; Del Connealy, Omaha District; Richard Kam, WES; Mike Warren, WES; Alan Hewitt, CRREL.

PROCEEDINGS OF THE SIXTH CORPS CHEMISTS MEETING

16-17 MAY 1989

Welcome

LTC Jack Stephens*

LTC Jack Stephens, Acting Commander and Director, US Army Engineer Waterways Experiment Station (WES), welcomed all attendees to the Sixth Annual Corps Chemists Meeting. He stated that his function was to facilitate groups with productive information for assistance in the programs at WES. He was delighted that WES had the opportunity to host the meeting again this year and that the meeting was so well represented. He felt the WES tour was important so that all the impressive things on station could be seen by everyone. He commented that chemists were in a growth industry.

LTC Stephens recently attended a Commander's conference with LTG H. J. Hatch where the importance of the technology of hazardous and toxic waste (HTW) was emphasized. The Corps already is working with the US Environmental Protection Agency on HTW projects, and the Base Closure Act (BCA) program will create new work in this area. The most positive influence of the BCA comes from the income of land sale. Unfortunately the land is contaminated with hazardous and toxic waste that must first be cleaned up. Therefore, Corps chemists are now becoming involved in cleanup.

* Acting Commander, US Army Engineer Waterways Experiment Station, Vicksburg, MS.

Water Quality and the Corps Chemists

Lynn Lamar, Headquarters, US Army Corps of Engineers

Policy for Corps operations is governed by Engineering Regulations or ERs. A number of different ERs were reviewed, such as ER-1110-1-8100, Laboratory Investigations and Materials Testing; ER-1130-2-415, Water Quality Data Collection, Interpretation and Application Activities; ER-1110-1-261, Quality Assurance of Laboratory Testing Procedures; ER-1110-1-263, Chemical Quality Management, Toxic and Hazardous Wastes; and ER-1180-1-6, Construction Quality Management.

A new engineering regulation has been introduced into the US Army Corps of Engineers. It is ER 1110-1-1401, Interlaboratory Testing Program for Chemical Analysis. The purpose of this regulation is to establish an interlaboratory chemical analyses testing program for Corps labs performing water quality, sediment testing, and related chemical analyses. This program is designed to increase the validity of Corps analytical data by improving accuracy and precision. It is applicable to all Corps District, Division, and research labs performing water quality and related chemical analyses.

The interlaboratory quality assurance/quality control (QA/QC) program offers several positive attributes: (1) it involves analyses of identical samples by multiple labs in order to assess the continuing capability, performance, and progress of each participating laboratory; (2) the collaborative testing of methodologies measures the performance of a method in terms of accuracy, reproducibility, and repeatability. This type of testing is the evaluation of an analytical method by the participating lab under actual working conditions by analyzing portions of carefully prepared homogenous samples.

The US Army Engineer Waterways Experiment Station, Analytical Laboratory Group (USAEWES-EE-A) is the coordinating laboratory. WES is responsible for preparing homogenous samples and distributing them to the Corps labs; providing report forms, methodologies, and other instructions; collecting the data; sending a report to the Corps lab; checking the standard deviations for discrepancies and maintaining the confidentiality of the laboratories.

Questions were then directed to Ms. Ann Strong, Chief, Analytical Laboratory Group, WES.

Q. Are samples spiked individually or in a vat?

A. Samples are spiked individually at trace levels. We feel there is less error associated with individual spikes. This way, if the spiking compounds are retained on the walls of the sample container, the container can be rinsed by the analyst to get a good recovery.

Q. Are you still sending natural samples for the soil samples?

A. Yes, we are.

Q. Do you suppose you can find a natural soil or sediment sample that is high in the compounds of interest?

A. Yes, we have a sample that is quite high in a number of the priority pollutants including metals, PCB, and base neutral/acid extractable compounds.

Q. What about the use of microwave digestion for metals analysis?

A. I don't deny that the microwave will provide good digestion. However, I wonder about comparability of the microwave data to the total recoverable methods approved by the US Environmental Protection Agency (USEPA) in SW-846.* Can we currently control the microwave digestions to obtain the same recoveries?

Q. What is the funding method for the testing program?

A. Each lab is responsible for funding their participation in the program. It is currently designed only for Corps labs.

Q. Can we pick and choose samples we will be involved with?

A. Yes, because not every lab has the capability to perform all analyses.

COMMENT: Many of the Districts are contracting a major portion of their water quality work.

COMMENT: In those cases we need to be very conscientious about oversight and we may want to issue quality control check samples from the Division labs.

Q. What about the use of USEPA's QA sample program?

A. The primary purpose of the Corps Interlaboratory Testing Program is to evaluate and improve the overall quality of data produced by the Division labs with interaction between WES and the participants. Also the program will be complementary to the Missouri River Division's validation process for Corps labs so that samples for hazardous and toxic waste work will not be duplicated. The USEPA does not currently provide soil or sediment samples for QA analysis.

Q. We are concerned about the limited number of chemists in the Division laboratories and the time that will be devoted to programs such as this. Where do we draw the line on participation?

A. I'm not sure that I have the answer. However, I will comment that it is amazing how well some labs can perform on spiked water samples and how poorly they will then do on a water, soil, or sediment with matrix interferences.

Q. Is it feasible to have some type of QA sample that can be introduced in the field to follow the samples through the entire process?

A. The theory is good, but it's not so easy to implement.

* US Environmental Protection Agency, Office of Solid Waste and Emergency Response. 1986 (Nov). "Test Methods for Evaluating Solid Waste," SW-846, 3rd ed., Washington, DC.

General Water Quality Problems: Audience Discussion

Chaired by Ann Strong, US Army Engineer Waterways Experiment Station

Communication between field managers and lab personnel is very important in water quality analyses. Usually the District is responsible for the collection of samples - either by District personnel or by contractors and the samples are sent to the Division labs for analysis. Too often the samples are poorly identified, there is insufficient sample for the requested analysis, and the field or District personnel fail to convey to the Division lab exactly what analyses they are requesting. In turn, the lab may proceed with a normal laundry list of analyses and fail to interact with the field to determine what is desired. In reverse, problems occur when the field crew is not aware of what the lab is going to do with the sample and may not collect enough sample or preserve it properly. Levels of communication should go down to people actually doing the work. The field should let the labs know where the sample is collected, how the sample was collected, and when the sample will be shipped to them so that lab time can be scheduled. The labs should also know what analyses they are expected to perform on the samples. In return the lab should quote a price range to the field for the work to be performed and a projected time when the analyses should be completed. A good form of communication is written documentation. Everything done by an individual on a project should be written down. An example of good documentation is the chain-of-custody procedures in practice.

There seems to be an overemphasis on hazardous and toxic waste (HTW) work by the Division labs and not enough on the importance of water quality work. Division labs should be aware that water quality analyses are as important to the Corps mission as HTW. Some of the District water quality people felt that their work is suffering as a result of Division lab emphasis on HTW work. The HTW and water quality work should complement each other rather than conflict. A lot of the procedures used for HTW work date back to the old US Environmental Protection Agency (USEPA) water quality procedures. There is a lot of good positive spin-off in both directions. They both deal with common contaminants. Both programs deal with environmental quality and trace amounts of pollutants, although in many cases they are more than trace quantities. An example of this interaction is a small dredging project in Alaska where a sampling plan based on HTW protocol was presented at an interagency meeting. As a result, the USEPA agreed to fund additional sampling and analyses. A lot of procedures and publications for HTW are photocopied out of EPA manuals from the 1970's for quality assurance (QA)/quality control (QC). HTW has leaned more heavily on QA checks, whereas water quality tended to rely on internal QC checks. Both are equally important.

The comment was made that Corps chemists need more exposure to water quality workshops. These are usually attended by engineers and biologists. Another comment was that communication needs to be a two-way street with more interaction between project managers and chemists. One attendee mentioned that the USEPA was adding to its list of priority pollutants. No one was aware of the status of this proposal or had a current update on this.

The use of QA samples in the HTW work has improved communication in these programs. Because of the necessity for checking these samples immediately upon receipt in a QA lab, improper collection, preservation, and documentation are immediately noted and this information is related to the field crew. Of course this cannot detect problems

between the prime contractor of an HTW project and his analytical lab. Frequently field people see only a very small portion of the contract requirements and the information contained there may not be complete; particularly if it only references documents as guidance.

In some cases the QA samples are the only samples that have reliability. It is not always feasible to resample a project. QA samples (duplicate samples from the field going to a QA lab in addition to the primary lab) are not usually part of water quality projects. For this reason we need to be very sure that the laboratory performing the analyses has all QC checks in place. Does this communication gap exist to the point that a lab may not even know that samples are coming in? Unfortunately it happens more often than we like to admit. Samples today appear to be more problem-oriented, whereas water quality work once tended to follow a set schedule. As we start to dredge some of the rivers and harbors that have not been dredged for several years, we will likely see more contaminant problems that do not fit the mold for routine water quality analyses.

A number of Corps projects at dams are using reaeration as a method for reducing volatile contaminants and the release of volatile compounds is perceived as being a problem.

What about laboratory certification such as that performed by the USEPA? There is a push on now for a national accreditation program. The only certification program that the USEPA has is for labs performing analysis for the Safe Drinking Water Act.

What about the Contract Laboratory Program (CLP) protocol? CLP is not a validation program. The USEPA specifically states that it is not a validation program. It is a contract program set up specifically for Superfund work. Some USEPA regional people were concerned that the Corps was going to use the CLP program and they expressed relief that the Corps had their own program for contracting and overseeing QA. In many instances, the USEPA has stated that CLP is not adequate for sediment testing for dredging programs, particularly in the area of PCB analyses.

The accreditation program as proposed by the American Association of Laboratory Accreditation (A₂LA) is probably not adequate for our purposes. Their current accreditation is a boilerplate more or less limited to reviewing facilities and personnel. They seem to be more interested in testing for manufactured processes at this point.

There is also another problem that we may need to address and that is the problem of highly contaminated samples coming in with no warning that high levels exist. At HTW sites, personnel usually have access to organic vapor analyzers to at least warn them of volatile organics. We have come across sites in the normal Corps projects where noxious chemicals were present and there was no access to monitoring devices to assist the field people. We need to better educate our own field people that the possibility of hazardous materials exists and to take proper precautions.

PCB Congener Toxicity

Victor McFarland, US Army Engineer Waterways Experiment Station

Polychlorinated biphenyls (PCBs) are widespread in the environment, persistent, and can cause adverse biological effects. They are among the neutral organic chemicals most frequently studied as sediment contaminants. However, many of the 209 possible PCB congeners have never been reported in environmental samples, are not toxic, or have low bioavailability. Analysis of PCBs as total PCBs or as Aroclors yields little information about the potential biological significance of the mixture of congeners in a sample. Study proves that nontoxic monochlorobiphenyls constituted as much as one-third of the total PCBs in samples of water, sediment, clams, and fish and if reported as total PCBs, would be considered potentially more toxic than warranted.

Congeners most likely to be of concern are the moderately chlorinated isomer groups having five to seven chlorine atoms per molecule. These congeners are generally metabolized and eliminated less readily than the lower chlorinated PCBs, but are more bioavailable than the highly chlorinated PCBs. Also, these moderately chlorinated groups were synthesized in high proportions in many commercial Aroclor formulations and are thus likely to be prevalent in the environment.

Chemical synthesis of all 209 PCB congeners has only recently been accomplished and the individual standards required for analysis are not readily available. Thus, it is neither practical nor desirable to specifically analyze all 209 congeners. It is proposed that a selected group of congeners be chosen for a congener-specific analytical protocol. Environmental prevalence, relative abundance in animal and human tissue samples, and potential toxicity are components of the rationale used for determining the importance of individual congeners. Based on this rationale, 36 specific PCB congeners are suggested for use in the evaluation of dredged material. Ongoing research at the US Army Engineer Waterways Experiment Station continues to focus on the ecological importance of PCB congeners.

PCB Congener Analysis

Newberry Brown, US Army Engineer Waterways Experiment Station

Aroclors are the designations given to commercially produced mixed polychlorinated biphenyls (PCBs), with the numbering system based on the percentage of chlorine in the mix. A particular Aroclor is a mix of PCBs in a specified ratio. When Aroclors are degraded environmentally or on purpose, or when there is a mixture of Aroclors, the use of a single Aroclor standard is not entirely adequate for identification or quantitation. Two attempts have been made to overcome this problem: (1) Aroclor mixes, and (2) individual PCB congeners. Aroclor mixes have been used, but are not adequate when degradation or leaching has occurred. Identification and quantitation of individual congeners largely overcome this problem.

The main problem, however, is to resolve all of the 209 possible congeners. Michael Mullens, a researcher for the US Environmental Protection Agency, used a 60-m DB5 column with hydrogen as a carrier gas and a very slow temperature rise to get good resolution. The problem with his procedure was that it took over 2 hr for each sample to be analyzed.

Not all 209 congeners are commercially available in standard mixes that can be used for identification and quantitation. Most of the standard mixes used by the Analytical Laboratory Group at the US Army Engineer Waterways Experiment Station (WES) were obtained from the National Research Council of Canada. WES used dual columns consisting of a 30-m DB5 column in conjunction with a 30-m SPB 608 (Supelco) column and an 80-min run time. Usually two mixes of about 12 congeners each for a total of 24 congeners were used. Depending on the requirements of the research project, an additional four mixes, for a gross total of 83 congeners, were used. A few of the congeners in the mixes were duplicates and some could not be resolved so that there were about 75 usable congeners. A computer program was set up to flag congeners not confirmed within set limits of quantitation by both columns.

PCB Cleanup Methods Study

Richard Karn, US Army Engineer Waterways Experiment Station

There are many possible sources of error in analysis of polychlorinated biphenyls (PCBs). These could include differences in standards, operator errors, methods of calculating Aroclor and total PCB concentrations, or the presence of interfering substances not removed during sample preparation. Studies conducted by different labs at a contaminated Chicago River sediment site yielded significant concentration differences. One distinction noted between studies was the use of differing cleanup procedures. Prior to quantification of PCBs in soil and sediment samples by gas chromatography (GC), extracts must be cleaned to remove interfering substances such as oil and grease and sulfur. Failure to remove such interfering substances can result in erroneous PCB concentration data.

In an effort to resolve the differences reported by laboratories on the Chicago River sediment, a study was performed at the US Army Engineer Waterways Experiment Station (WES) on the effect that cleanup procedures for removing oil and grease and sulfur had on PCB data. The extractions were done by soxhlets with hexane/acetone as the solvents. Two composite samples from the Chicago River were studied.

Four different cleanup procedures were utilized. They were (1) florisil and mercury, (2) silica gel and mercury, (3) sulfuric acid and mercury, and (4) sulfuric acid and tetrabutylammonium-sulfite reagent (TAS). The two composited samples were air dried and ground up, sieved, and mixed to assure homogeneity. The samples were replicated five times for each cleanup procedure. The results are shown in Tables 1 and 2.

In conclusion, from the data obtained, the silica gel/mercury gave the best cleanup. It removed a substantial amount of both oil and grease and sulfur from the samples. Results from this study did not produce statistically different quantitation results for PCBs using the different cleanup procedures. This may be due to improved GC columns that provide better resolution of peaks.

Table 1

Concentrations [mean (standard error)] of Total PCB, Oil and Grease Prior to and Following Cleanup, Sulfur Prior to and Following Cleanup, and Percent Recovery of Added PCB for Composite Sample 2

Treatment	PCB, mg/kg	Oil and Grease, mg/kg		Sulfur, mg/kg		% Recovery
		Before Cleanup	After Cleanup	Before Cleanup	After Cleanup	
Florosil	21.9 (1.7)ab*	2,704 (79)a	1,868 (69)a	13.4 (0.4)b	4.3 (1.3)a	90.3 (2.8)a
Sulfuric/TAS	26.6 (1.3)a	2,326 (36bc)	1,622 (81)b	11.5 (1.2)b	0.6 (0.07)b	95.8 (18.2)a
Sulfuric/Hg	22.0 (1.5)ab	2,558 (56)ab	1,514 (62)b	15.9 (0.6)a	5.4 (1.1)a	65.5 (4.0)a
Silica gel	20.2 (2.2)b	2,280 (121)c	422 (32)c	16.0 (0.6)a	0.7 (0.2)b	75.6 (0.3)a

* Means for a parameter followed by the same letter are not statistically different.

Table 2

Concentrations [mean (standard error)] of Total PCB, Oil and Grease Prior to and Following Cleanup, Sulfur Prior to and Following Cleanup, and Percent Recovery of Added PCB for Composite Sample 2

Treatment	PCB, mg/kg	Oil and Grease, mg/kg		Sulfur, mg/kg		% Recovery
		Before Cleanup	After Cleanup	Before Cleanup	After Cleanup	
Florosil	8.20 (1.68)a*	926 (33)b	618 (31)a	6.58 (0.47)a	3.10 (0.20)a	75.0 (0.00)b
Sulfuric/TAS	6.98 (0.50)ab	916 (74)b	420 (31)b	4.04 (0.21)b	0.14 (0.02)c	77.7 (12.1)b
Sulfuric/Hg	3.90 (0.53)b	950 (54)b	446 (43)b	4.08 (0.37)b	1.52 (0.61)b	122.2 (10.0)a
Silica gel	8.06 (1.34)a	1,248 (21)a	584 (12)a	3.62 (0.51)b	0.22 (0.02)c	84.7 (1.39)b

* Means for a parameter followed by the same letter are not statistically different.

Temperature-Programmed Analysis of PCBs Using Megabore Columns

Anand Mudambi, New England Division

The New England Division basically uses method 8080 from SW-846* for the analysis of polychlorinated biphenyls (PCBs). The liquid/liquid extraction with methylene chloride is used for water and the soxhlet extraction with hexane is used for sediment/soil. Activated copper (treated with dilute nitric acid) is used for sulfur cleanup and florosil is used for basic extract cleanup. On a Hewlett Packard 5890 gas chromatogram, a good temperature program to consider when studying total PCBs is to have a 2- μ L sample injected onto a 250^o C injector. The oven will have an isothermal temperature of 170^o C being raised at 6^o C/minute to 270^o C until all compounds elute. Nitrogen is used as the column and make-up gas, although helium is best for the column. The DB1 and DB5 megabore columns are very reproducible for PCBs and pesticides. These columns are used as confirmation columns also. Spike recovery is normally 75-85 percent.

* US Environmental Protection Agency, Office of Solid Waste and Emergency Response. 1986 (Nov). "Test Methods for Evaluating Solid Waste," SW-846, 3rd ed., Washington, DC.

Influence of Groundwater Well Casings On Organic and Inorganic Analytes

Alan Hewitt, US Army Cold Regions Research
and Engineering Laboratory

Stainless steel 316 well casings are compatible with organic analytes because there is little interaction. Most organic analyses are done inside controlled glassware with Teflon tops. Resource Conservation and Recovery Act wells should be (1) fluorocarbon resins (Teflon) or (2) stainless steel (PVC, PTFE, SS316, or SS304) for monitoring volatiles. Two possible interactions could be adsorption of analyte or desorption of sorber analytes inside an SS casing. Lead is readily absorbed in the stainless steel casings. Teflon casings work better with inorganics and stainless steel for organic analytes. In well casings, a low pH causes high corrosion and a high pH might cause a low corrosion. Below are some comparative results using inorganics in stainless steel:

<u>Type</u>	<u>AS</u>	<u>CD</u>	<u>CR</u>	<u>PB</u>
SS316	Sorption	Leached	Sorption	Sorption
SS304	Sorption	Leached	No effect	Ext Sorp.

Matrix Interferences in Analysis for Nutrients, Metals, etc.

Don Brown and Mike Warren, US Army Engineer Waterways Experiment Station

Selenium is one of the most difficult elements to measure. When analyzing a sample for selenium using the hydride method, excess chlorine or chloride presents a major interference as reverse oxidation occurs. The problem can be corrected by bubbling nitrogen into the sample during digestion. This process eliminates the extra chlorine or chloride and maintains the integrity of the sample. Ninety-three hours after digesting without nitrogen bubbles, an 18-percent recovery was obtained. After bubbling with nitrogen, a 95-100 percent recovery was obtained.

Selenium is one of the metals most often missed in the audit samples sent to the laboratories. It is not known whether it is the chloride causing interferences or operators not being able to compensate for interferences. The US Army Engineer Waterways Experiment Station (WES) has gotten more consistent results with selenium by using the Zeeman background correction graphite furnace atomic absorption (GFAA) method.

Nickel nitrate in combination with magnesium nitrate is a good matrix modifier for selenium when using a graphite furnace. It has been proven by Perkin Elmer that the combination gives better and more consistent results than using nickel nitrate alone. However, for arsenic analysis only the nickel nitrate is used. Palladium was also investigated at WES, but results were not nearly as good. Some other Corps chemists reported successful use of palladium as a modifier for mercury, arsenic, and selenium. Sulfate interference has also been reported as a problem, particularly in sediment samples. Small variation in sulfate will produce serious interferences in selenium. This problem is usually solved by varying parameters (gas flows, temperatures, etc.). Frequently dilution of a sample will eliminate interference problems. Sulfate interference is one problem that does not respond well to Zeeman correction.

In nutrient analyses, interferences can sometimes be eliminated by changing the wet-chemistry process. For example, some samples that showed negative peaks for ammonia using the alkaline phenol method were run successfully using dialysis chemistry. The problem with using dialysis was that detection limits were not low enough to quantitate many of the samples.

Chemical interference is another common matrix problem in GFAA. It is generally caused by a component in the sample that is thermally stable with the analyte of interest. The first approach to solving chemical interference is usually dilution. If this is not successful, then matrix modifiers are investigated. The need for a matrix modifier is usually determined by the results from matrix spikes indicating either signal enhancement or depression. Matrix modifiers either (1) stabilize or lower the disassociation temperature of the thermally interfering compound or (2) stabilize the analyte by increasing the char temperature and allowing the interference to burn off first. WES's experience with saltwater samples indicates that the normal modifiers currently recommended by Perkin-Elmer do not work. Better results were obtained using ammonium nitrate, one of the earliest modifiers used for graphite furnace work.

Matrix matching is another method which can be used to compensate for matrix interferences. It is most successful when the origin and general composition of the sample are known. Unfortunately, this is usually not the case.

The Zeeman background correction used in conjunction with the L'Vov platform in the graphite furnace enhances the laboratory capability in terms of achieving lower sensitivity for problem samples. The Zeeman effect is a less time-consuming avenue to quality answers because it has a more resolute energy source. The lamp emits a wavelength through the furnace for the element of interest and a large electromagnet splits the light component into two parts. The sigma portion of the light source is the main concern because it gives the element a more resolute light to be absorbed and a lower sensitivity, therefore better results are obtained. Additionally the use of the L'Vov platform allows the samples to be deposited onto it and it is primarily heated by radiation from the walls of the graphite tube. Modifying the normal temperature program elevates the drying temperature and results in an elevated charring temperature when the sample is atomized. When using elevated temperatures, interferences are burned off because the resident time of the inert gaseous phase is shortened and interferences are separated from the element of interest.

The method of standard additions is also useful when looking at low concentrations of metals with interferences. One chemist suggested that one plus zero is probably good enough for most samples but the Contract Laboratory Program protocol requires three points plus zero.

Q. Does the acetic acid in the extraction procedure (EP) toxicity procedure affect the metals determination?

A. The procedure calls for a nitric acid digest of the EP toxicity sample. The acetic acid is probably eliminated in the digestion process.

The Chemist Intern Program

Bruce Heitke, Headquarters, US Army Corps of Engineers

At the 1988 Corps Chemists Meeting and at several Superfund line item reviews, concern was expressed over the ability of the Corps to recruit and retain quality chemists. An overall survey by the Office of Personnel Management (OPM) determined that there was not a problem with recruiting.

There are several ways of attracting good people - (1) Special salary rate (difficult to obtain), (2) Intern Training Program, and (3) Direct hire. Susan Haines, OPM, conducted a Health, Science, and Technology Job Fair making use of direct hire authority. The Corps was able to get a couple of chemists through this program.

Susan Haines then drafted a Master Intern Training Plan (MITP) for chemists, GS-1320 series. The MITP is a comprehensive plan which outlines the Corps subject matter that chemist interns should know by the time they reach their target grade. The MITP may be modified to fit the needs of the particular employing Field Operating Activity (FOA). The supervisor will use the MITP as a guide when developing an individual development plan (IDP) for each intern.

The MITP supports noncompetitive promotion to a target grade of GS-11 when all requirements are met. It provides for accelerated training which will lead to accelerated promotion of the intern. The length of training varies according to the entry qualifications of each intern. The chemist MITP has two entry levels, (1) interns who enter the program as a GS-1320-5 will complete a two-phase minimum 30-month training program and, (2) interns who enter the program as a GS-1320-7 will complete a two-phase minimum 18-month training program.

Phase I is designed to give the intern an understanding of the mission and operation of the Army, Army major commands, the Corps of Engineers, and the employing FOA. The intern is oriented on policies and procedures that guide performance of work. Training is designed to provide experience in the application of analytical concepts, principles, and techniques. A combination of on-the-job and formal classroom training is involved. Phase II is 1 year of training designed to give the intern the advanced technical classroom training and on-the-job experience necessary to become a fully qualified journeyman chemist.

The IDP is a written plan that is used to prepare the intern for target-level performance. The supervisor, with input from the intern, will develop the IDP by comparing the intern's education and experience with the requirements shown in MITP. Based on that comparison, the supervisor will tailor the MITP to the intern. When the intern does not have job-related experience, the entire MITP becomes the intern's IDP. The MITP may be modified to meet the target level job requirements of local interns.

DISCUSSION:

The Career Intern Program as proposed has not been well-received by most of the Corps FOAs. They feel that the program is primarily designed to benefit the Missouri River Division (MRD) facility and will not provide the FOAs with the support that they need. They feel that they should be able to design the training program to fit their specific needs and that only minimum time would need to be spent at the MRD facilities.

Influence of Soil Sampling and Soil History in Investigating Soil-Mediated Processes

Charles "Mike" Reynolds

US Army Cold Regions Research and Engineering Laboratory

As an introduction, soil should be viewed as dynamic, alive, and active - not inert. The statue of soil has influence on many processes. A range of properties were looked at, such as organic matter, texture (clay), pH, and cation exchange capacity with the objective of obtaining a sample history. To separate the biological effects, soil was separated by sterilization. An air-dried sample was used as a control. Other samples were oven dried, irradiated with Cobalt-60, treated with propylene oxide, and autoclaved 3x, 2x, and 1x, and with mercuric chloride. A soil network exchange is being established. A 5-gal (18.9-cubic decimetre) bucket of sample is needed, together with all known properties.

USATHAMA - The New Corps Element - Programs and Interactions

Marty Stutz, US Army Toxic and Hazardous Materials Agency

The US Army Toxic and Hazardous Materials Agency (USATHAMA) started with the Corps in 1988. It has three missions: (1) installation and restoration, (2) base closure, and (3) the compliance mission. The missions haven't been explained in detail. The base closure mission is probably going to be an accelerated installation and restoration program. USATHAMA will expand from an agency of 90 people in April 1989 to an operation of about 150 authorized people on 1 October 1989. USATHAMA as an agency has tried to get the US Environmental Protection Agency's (USEPA's) support, but the USEPA does not think the agency has the capacity.

The organization is set up with a number of divisions. There is a Compliance Division that handles the Resource Conservation and Recovery Act issues, a Base Closure Division that is working on 14 base closure operations starting this year, an Installation/Restoration Division that has been working with the Corps over the years, and the Technology Division, where most of the chemists are located.

The Technology Division consists of three branches. The Analytical Branch is responsible for all of the chemistry support to all of the USATHAMA missions. The Process Development Branch has to do with the treatability, pollution abatement, R&D efforts, incineration, decontamination, composting, and method development such as explosive analyses, etc. The Environmental Branch has input into the interpretation of the environmental regulation requirements. This branch also has an environmental hotline with an 800 number that answers questions 24 hr a day.

USATHAMA also has a reference material program. They develop top quality analytical reference materials for use in labs as primary standards. The reference material repository is now combined with the USEPA repository located in Research Triangle Park, North Carolina. In addition, there is an explosive reference material repository at the Picatinny Arsenal in New Jersey. These are primary standards that are traceable to the National Institute of Standards and Technology and are available upon request to laboratories at no cost as part of the mission of USATHAMA. Information about standards can be obtained from Darlene Bader at (301) 671-3348/3206. The normal time to fill an order is about 2 weeks - but for explosives it's anybody's guess.

USATHAMA is very automated as far as the data management area goes. All data come into the agency electronically. There is a routine checking procedure that involves reviewing the data and checking to see if samples are analyzed within acceptable range, holding times, QC samples, and parameters analyzed.

A few of the R&D effort studies done at USATHAMA are bioremediation studies, hot gas decontamination of structures, air stripping for volatiles, and analyses for explosive materials.

There is a memo in preparation for LTG H. J. Hatch's signature titled "Policy Guidance on Sampling and Chemical Procedures Used for the Installation Restoration Program." The memo defines policy to be used by the Corps for Installation Restoration Programs and recommends the adoption of Contract Laboratory Program (CLP) procedures to the extent possible for these programs. Procedures shall include but not be limited to field

sampling audits, laboratory audits, the use of CLP analytical methods where available, the analysis of performance evaluation samples, the review of data and data packages to assure CLP requirements are met, review of data packages to determine technical usability and the acquisition and retention of all data package documentation.

DISCUSSION:

Concern was expressed over the use of CLP versus SW-846* procedures and why there was a need for using the different procedures for different projects when they provide the same basic data. Primary differences are in the quality assurance/quality control (QA/QC) requirements. None of the Corps offices other than USATHAMA appeared to have been consulted concerning the use of CLP. It was not known what review the memo had received and it was reemphasized that this was only for Defense Environmental Restoration Account (DERA)-funded Installation Restoration Programs. Depending on the driving regulation at a cleanup site, methods may be CLP, SW-846, or the new 500 series required for drinking water. The CLP requirements are definitely "overkill" at some of the site investigations being done for the military and will drive up the costs tremendously.

* US Environmental Protection Agency, Office of Solid Waste and Emergency Response. 1986 (Nov). "Test Methods for Evaluating Solid Waste," SW-846, 3rd ed., Washington, DC.

Sediment Analysis Case Studies

Dave Bowman, Detroit District

In a study performed by Dave Bowman on sediment samples from Manistique, MI, data indicated that very different results could be obtained from the same set of samples using essentially the same analysis methods. Samples were originally sent to Thermo-Analytical/ERG, Inc. for analysis of polychlorinated biphenyls. Because the values were so high for some samples and had such a wide range of results for the various locations, the US Army Engineer Waterways Experiment Station (WES) was asked to analyze aliquots of six of the samples and to arrange for additional analysis by a third laboratory. WES arranged for third party analysis by the Tennessee Valley Authority. Results are presented in Table 1. All three labs identified 1248 as the Aroclor, but the concentrations obtained for aliquots from the same samples were very different. Samples were mixed in the wet state using the procedure described in SW-846,* but because the samples contained rocks, sticks, and wood pulp, it was impossible to obtain a truly homogeneous sample. Therefore, it was virtually impossible to duplicate results within a lab and even less likely to replicate among labs.

* US Environmental Protection Agency, Office of Solid Waste and Emergency Response. 1986 (Nov). "Test Methods for Evaluating Solid Waste," SW-846, 3rd ed., Washington, DC.

Table 1
Manistique, Michigan
PCB Concentrations as Aroclor-1248
mg/kg (dry weight)
August, 1988

	<u>TMA/ERG</u>	<u>WES</u>	<u>TVA</u>
1	0.89		
1A			
2	0.28		
3	1.00	1.19(2)	0.19
3A	21.0	93.00(2)	2.20
4	0.11		
5	0.13		
5A	660.00	224.50(2) 63.50(2)	18.0
5B			
6	<.10		
6A	0.03		
6B	7.10		
6C	4.90	9.05(2)	1.20
7	3.00 1.90*		
8	0.37		
8A	6.80		
8B	0.44		
8C			
8D	5.80		
9	31.00	26.35(2)	3.40
10	25.00* 9.00		
11	<40		
12			
12A	550.00	88.00	44.00

TMA/ERG - ThermoAnalytical/ERG, Inc.

WES - US Army Engineer Waterways Experiment Station.

TVA - Tennessee Valley Authority.

(2) - Average of two analyses.

* - These two values were reported as Aroclor-1254.

QA/QC Reports for HTW Projects

Richard Kissinger, Missouri River Division

The purpose of quality assurance (QA) is to ensure that the contractor is producing reliable data that can be used to make site decisions. The QA/quality control (QC) reports consist of a cover letter, report narrative, and data comparison tables. The report narrative should include a summary, QC data discussion, QA/QC data comparison discussion, other problems (chain-of-custody, preservative, shipping, etc.) and corrective actions by contacting the project manager. The completed reports are sent to the Corps of Engineers project manager. Discussions with the project manager before the project starts and after the QA/QC report is completed are beneficial to everyone.

The report is generated from sample receipt information, QA laboratory data, and contractor's laboratory data. Many problems occur in preparing the report, such as matching the sample's ID, trip blanks, and rinsates. Upon receiving the samples, they should be checked for broken samples, correct preservation, proper containers, chain-of-custody labels, and complete data sheets. The holding time specification is another important factor of the report.

The data requirements for a QA/QC report are: blanks, lab duplicates, field duplicates, matrix spike recoveries, matrix spike duplicates, surrogate recoveries, trip blanks, and rinsates. The acceptable limits for matrix spikes are given in Table 1.

Table 1
QC Limits for Duplicated and Matrix Spike Recoveries

<u>Fraction</u>	<u>Compound</u>	<u>QC Limits*</u> <u>*RPD</u>	<u>Water</u> <u>Recovery</u>	<u>QC Limits*</u> <u>*RPD</u>	<u>Soil</u> <u>Recovery</u>
VOA SMO Sample No.	1,1-Dichloroethane	14	61-145	22	59-172
	Trichloroethene	14	71-120	24	62-137
	Chlorobenzene	13	75-130	21	60-133
	Toluene	13	76-125	21	59-139
	Benzene	11	76-127	21	66-142
B/N SMO Sample No.	1,2,4-Trichlorobenzene	28	39-98	23	38-107
	Acenaphthene	31	46-118	19	31-137
	2,4-Dinitrotoluene	38	24-96	47	28-89
	Pyrene	31	26-127	36	35-142
	N-Nitrosodi-n-Propylamine	38	41-116	38	41-126
	1,4-Dichlorobenzene	28	36-97	27	28-104
Acid SMO Sample No.	Pentachlorophenol	50	9-103	47	17-109
	Phenol	42	12-89	35	26-90
	2-Chlorophenol	40	27-123	50	25-102
	4-Chloro-3-Methyl Phenol	42	23-97	33	26-103
	4-Nitrophenol	50	10-80	50	11-114
Pest SMO Sample No.	Lindane	15	56-123	50	46-127
	Heptachlor	20	40-131	31	35-130
	Aldrin	22	40-120	43	34-132
	Dieldrin	18	52-126	38	31-134
	Endrin	21	56-121	45	42-139
	4,4'-DDT	27	38-127	50	23-134
Metals		20	75-125	20	75-125

* Relative percent difference.

Petroleum Hydrocarbon Methods

Mike Woster, Missouri River Division

There are many analytical methods available for identifying petroleum hydrocarbons. The more commonly used methods are gas chromatography (GC) or a combination of methods. The more commonly requested identifications are for crude oil, JP 4, J-P 8, gasoline, and No. 2 fuel oil. There are official methods from the American Society for Testing and Materials (ASTM) and the US Environmental Protection Agency (USEPA) as well as "modified" methods. The Missouri River Division (MRD) lab has their own "in-house" methods. Table 1 lists over two dozen available methods for identifying petroleum hydrocarbons and refers to pertinent literature that is listed on pages 25 and 26.

At MRD, total recoverable petroleum hydrocarbon (TRPH) extractions are done by method 418.1 along with infrared (IR) or a "modified" 8015 method. Fuel identification is done by ASTM D3328-78 and GC-flame ionization detector (FID) or ASTM D3650-78 and fluorescence. A modified 8015 (along with headspace and FID) or USEPA 8240 (along with purge and trap on the GC/mass spectrometer (MS)) is used to identify benzene, toluene, ethylbenzene, and xylenes (BTEX). Table 2 summarizes some of the methods investigated by MRD.

Weathering (evaporation, degradation, and separation), non-aqueous product layers (NAPL), reporting results, and regulatory requirements are some of the problems encountered when working with petroleum hydrocarbons.

Although there are any number of procedures for analyzing various petroleum components, there doesn't seem to be any well-defined set of procedures for sampling. Analyses of these petroleum products and comparisons between samples may vary widely.

Table 1
Analytical Methods Available for
Petroleum Products

Agency	No. #	Product	Reference
	503F	Oil and grease analysis - hydrocarbons	APHA, AWWA, WCPF 1980
USEPA 600-4-79	413.1	Oil and grease, total recoverable from water/ separatory funnel extraction	USEPA 1979
	413.2	Oil and grease, total recoverable from water/ separatory funnel extraction	USEPA 1979
	418.1	Petroleum hydrocarbon - total recoverable	USEPA 1979
USEPA SW-846	9070	Total oil and grease analysis	
	9071	Oil and grease extraction from sludge	
	5030	Volatile organics in soil	
USEPA 40 CFR 136	601	Purgeable organic halocarbons	USEPA 1984
	602	Purgeable organic aromatics (BETX)	USEPA 1984
	624	Purgeable organic + 10	USEPA 1984
	625	Base/neutrals and acids + 25	USEPA 1984
USEPA 40 CFR 141	503.1	Purgeable aromatic and unsaturated organics	USEPA 1987
USEPA	239.2	Determination of lead	USEPA 1979
California WCB	9/85	Guideline for addressing fuel leaks	Eisenberg et al. 1985
Florida	17-70.008	Petroleum contamination - site cleanup criteria, contamination assessment	State of Florida 1987
US Coast Guard	CG-D 52-77	Oil spill identification system	Bentz 1977
NJDEP	87-5	Water-soluble phase of gasoline	Kramer and Hayes 1987b
NJGS	87-4	Water-soluble phase of fuel oil #2	Kramer and Hayes 1987a

Table 2
Summary of Petroleum Hydrocarbon Procedures Used at MRD

Method	Matrix	Sample Preparation	Detection	Qnt.	Detection Limits	Comments	
						Advantages	Disadvantages
418 9071/418.1	Water	Freon 113	IR, 2930 cm^{-1}	Y	0.2-1.0 ppm	1. Standardized; good for comparisons.	1. Artificial reference.
	Soil	Ext'n/silica gel	IR, 2930 cm^{-1}	Y	25-100 ppm	2. Not dependent on fuel type or weathering.	2. False positives, interferences. 3. Results commonly 100-200 higher than other methods. 4. No identification of fuel. 5. Volatiles are lost.
ASTM D3328	NAPL	Dilute w/ CS_2	GC-FID	N		1. Fingerprint identification of fuel type. 2. Weathering effects.	1. Not quantitative.
ASTM D3659	NAPL	Dilute w/cyclohexane	Fluorescence	N		1. Quick characterization. 2. Works best for heavier fuel mixtures which don't chromatograph well.	1. Not quantitative. 2. Poor response to gasoline.
MOD 8015 CAL L.U.F.T.	Water	Headspace after 1 hr. @ 90° C.	GC-FID	Y	10-50 ppb	1. Clean-only volatiles injected.	1. Volatiles only-rapidly decreased sensitivity > C.
	Soil	Add water, then same.	GC-FID	Y	10 ppm	2. Provides identification and quantitation.	2. Temperature dependent.
MOD. 8015	Water	Liq/liq ext'n	GC-FID	Y	50 ppb	1. Can quantitate to > C25 if necessary.	1. Volatiles are lost.
	Soil	Sonication	GC-FID	Y	10 ppm		2. Extractable nonvolatiles can contaminate system.
MOD. 8015	Water	Heat @ 90° C 1 hr. Inject 1 ml HS.	GC-FID	Y	50 ppb fuel 1 ppb BTEX	1. Clean-only volatiles. 2. Identification and quantitation.	1. Low sensitivity as volatility decreases. 2. Temperature dependent.
	Soil	Mix with Na_2SO_4 . Sonicate with CS_2 in water bath.	GC-FID	Y	10 ppm fuel 1 ppb BTEX	1. No loss of volatiles. 2. Identification and quantitation. 3. Quick and simple.	1. Extractable nonvolatiles can contaminate system.

References

American Public Health Association, American Water Works Association, Water Pollution Control Federation. 1980. Standard Methods for the Examination of Water and Wastewater, Washington, DC.

Bentz, A. P. 1977. "Oil Spill Identification System," US Coast Guard R&D Center, GC-D-52-77.

Eisenberg D. M., Oilver, A.W., Johnson, P. W., Tempelis, D.S. 1985. "Guidelines for Addressing Fuel Leaks," California Regional Water Q.C. Board, San Francisco Bay Region.

Kramer, W. H., and Hayes, T. J. 1987a. "Water Soluble Phase of Gasoline: Results of a Laboratory Mixing Experiment," N.J.-DEP-DWR, New Jersey Geological Survey Technical Memorandum 87-4.

Kramer, W. H., and Hayes, T. J. 1987b. "Water Soluble Phase of Gasoline: Results of a Laboratory Mixing Experiment," N. J.-DEP-DWR, New Jersey Geological Survey Technical Memorandum 87-5.

State of Florida. 1987. "Petroleum Contamination Site Cleanup Criteria," Florida State Regulation, 17-70.002.

US Environmental Protection Agency. 1979. "Methods for Chemical Analyses of Water and Wastes," Revised 1983, EPA 600-14-79-020.

US Environmental Protection Agency. 1984. "Guidelines Establishing Test Procedures for the Analyses of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," Federal Register, 40 CFR, Part 136.

US Environmental Protection Agency. 1987. Federal Register, 40 CFR, Parts 141 and 142.

Bibliography

American Society for Testing and Materials. 1984. "Water (II)," Volume 11.02. Annual Book of ASTM Methods, Philadelphia, PA.

Curtis, M. L. 1977. "Use of Pattern Recognition Techniques for Typing and Identification of Oil Spills," US Coast Guard, CG-D-38-77.

Frank, U., Stainken, D., and Gruenfeld, M. 1979. "Method for the Source Identification and Quantification of Oil Pollution," Proceedings of the 1979 Oil Spill Conference, Los Angeles, CA, Academic Press, Inc., New York, pp 323-331.

Kane, M. 1987. Manual of Sampling and Analytical Methods for Petroleum Hydrocarbons in Ground Water and Soil, Publication No. 4449, Academic Press, Inc., New York.

Kawahara, R. K. 1972. "Characterization and Identification of Spilled Residual Fuel Oils, by Gas Chromatography and Infrared Spectrophotometry," Journal of Chromatography Science, Vol 10., pp 629-636.

US Environmental Protection Agency, Office of Solid Waste and Emergency Response. 1986 (Nov). "Test Methods for Evaluating Solid Waste," SW-846, 3rd ed., Washington, DC.

Warner, J. S. 1978. "Chemical Characterization of Marine Samples," American Petroleum Institute Publication No. 4307.

Chemical Data Quality Management Responsibility, USACE HTW Work Plan

Bruce Heitke, Headquarters, US Army Corps of Engineers

Chemical Data Quality Management (CDQM) activities are required to ensure that the quantity and quality of chemical data necessary to make important decisions at each step in hazardous and toxic waste (HTW) projects are available in a timely manner. In some cases, the amount and quality of data may be dictated more by legal requirements than by requirements for HTW design purposes. To accomplish this objective, CDQM ensures that environmental samples are collected, transported, and analyzed according to established protocols and that data quality meets project requirements. Engineer Regulation 1110-1-263 (Appendix A, Ref. 16) and supplemental policy guidance (Appendix A, Ref. 17) describe CDQM responsibilities for all HTW activities conducted by the US Army Corps of Engineers (USACE) for Superfund and Defense Environmental Restoration Program (DERP) projects.

Within the Corps, CEEC-E, acting through CEEC-ER, has responsibility for CDQM requirements and other supporting issues related to the proper implementation and execution of all phases of HTW program activities under USACE management. As the USACE HTW design center, the Missouri River Division has primary responsibility for implementation of CDQM requirements for all aspects of HTW activities conducted in support of the Superfund Program, DERP, and non-mission HTW assignments.

Q. In the rewrite of the document, will there be any reference to the Department of Energy (DOE) and the work being proposed for them, particularly in the areas of mixed waste and low-level waste? Will we have an interagency agreement with DOE, the US Environmental Protection Agency (USEPA), and USACE?

A. One of the USACE initiatives at this time is to pursue HTW work, including that generated by DOE. Probably 85 percent of the DOE cleanup problems are HTW rather than radiation waste. These of course would require adherence to USEPA regulations. It is doubtful that the USEPA would be a party to an interagency agreement between the Corps and DOE.

Q. What about the reference to low-level waste in the documents relating to leaking underground storage tanks?

A. An effort was made to delete that terminology from the later documents and refer to containerized waste. The use of the term "low-level waste" is a misnomer because many of the tanks may contain waste that is not highly regulated, yet may be high in concentrations of some products.

Proposed Revisions, ER 1110-1-263

Marcia Davies, Missouri River Division

The revision of Engineer Regulation (ER) 1110-1-263 was initiated in Washington and passed on to the Missouri River Division (MRD). The revision process has been going on for about a year. Copies were sent out to the MRD Districts, Washington, and other Division labs for comments. Currently a draft revision is being worked on to be sent to all labs that work with hazardous and toxic wastes.

Five appendixes have been added to the ER. The first appendix is a description of how the program works in terms of chemistry. *It outlines what the project managers do, what the Division labs do, what the construction officers do, and when things happen.* With respect to QA operations one of the things that has been added is a table which requests QA assignments. We expect one to be initiated with each project. The form that is to be filled out will outline the work that is to be performed, who will perform it, and the approximate costs. Appendix B is an outline of the procedures used for commercial lab validation. Appendix C is a guide to the preparation of the Chemical Data Acquisition Plan. Appendix D discusses the chemical quality assurance (QA) operations and responsibilities. The QA lab reviews documents, checks the samples, notifies project managers of problems, assures analyses (in-house or under contract) of the samples according to required methods, checks to be sure contractor's requirements are met, and writes the QA report.

In conclusion, the revised ER is an accurate description of how MRD has been operating for the last several years. There have not been any major changes in operations in the revised ER.

Comment: Lab people should be doing the actual inspections of the commercial labs as opposed to the chemical review people.

Response: There is a problem with having lab personnel available to do the inspections. If a problem is anticipated in a specific area, then every effort is made to get a lab person to join in the inspection. It should be pointed out that with the exception of total recoverable petroleum hydrocarbons, all audit samples are prepared and sent out by the US Army Engineer Waterways Experiment Station (WES). WES lab chemists coordinate the analyses and data generation with the contract labs. WES provides technical assistance to the laboratories to resolve analytical problems.

Chemistry Work Involved With Underground Storage Tank Removal

Lance Hines, Omaha District

The biggest problem that has been encountered in waste tank investigation is soil contaminants. Knowing what procedures to use for tank sampling is a great dilemma because very poor records have been kept on them. On sites where tanks are removed, there are unanswered questions about the volume of contaminants released, location of the release, and the hazardous waste involved. Soil samples, along with sensory screening, are the methods most used for testing the tanks. The cleanup levels vary from state to state. In Nevada, there is a specific cleanup level for tanks containing petroleum. The US Environmental Protection Agency (USEPA) 624 or 8015 method is used if contaminants are suspected in drinking water. In Arizona, if the petroleum level or contaminant level is 100 ppm, the soil is dug up. In California, if the level is between 100-1,000 ppm, the soil is only discussed.

Omaha District normally recommends the following analysis for underground storage tank removal: total recoverable petroleum hydrocarbons (TRPH), volatile analyses, and lead. Five samples for each analysis are requested. Composite sampling is not recommended.

Dilemma of Non-Aqueous Phase Liquid in Groundwater Sampling

Lance Hines, Omaha District

JP4 jet fuel, diesel oil, or gasoline is typically found as the non-aqueous liquid phase floating on groundwater. Sometimes special devices are used to go below the non-aqueous phase and collect only the groundwater for analyses. In some cases, the floating products are tested along with the groundwater, and in some cases the phases are analyzed as two separate samples. Testing the floating phase helps to determine whether contaminant levels are a problem.

There needs to be some guidance developed for sampling and analyzing these types of samples. Without such guidance there is no way to reproduce or compare analytical results within a sampling site or between sampling sites.

Soil Sorption and Plant Uptake of TNT

Judy Pennington, US Army Engineer Waterways Experiment Station

The objectives of this study were to (1) quantify the rate and extent of adsorption and desorption of TNT to soils, (2) determine what soil characteristics are associated with adsorption of TNT and its degradation products, and (3) determine the effects of pH and redox potential on the adsorption and desorption of TNT in soils. TNT and many of its degradation products are known to be toxic to fish and other aquatic fauna and can inhibit plant growth. TNT and its degradation products may be irreversibly adsorbed to soils and sediments. In a previous study using labelled compounds, comparison of ^{14}C recovered from ^{14}C -treated soils by solvent extraction and by a complete combustion technique showed that approximately 20 percent of the TNT was not accounted for. This showed irreversible adsorption or slow desorption of TNT and/or its degradation products.

In this study, TNT was shown to reach a steady state of adsorption after 2 hours of contact. Desorption also reached steady state within 2 hours, with almost half of the adsorbed TNT being removed. TNT adsorption correlated most highly with cation exchange capacity, extractable iron, clay content, and percent organic carbon. Sequential desorption indicated that almost all of the adsorbed TNT was desorbed after three sequential desorption cycles. Therefore soil sorption will not effectively prevent mobility of TNT in the environment unless adsorption increases over extended periods of time or more strongly adsorbing decomposition products are formed.

Quality Assurance - What Can We Do To Improve It?

Audience Discussion

Ways to improve quality assurance data for Division labs, in-house, and for contracting labs:

1. Field spike samples.
2. Give details of procedures used when sample is done.
3. Have access to software or on-line journal.
4. Chemical data newsletter from the Missouri River Division.
5. Regular standard operating procedure sessions of regulatory lab quality management (in-house).
6. Access to more standard reference material.

Plans for 1990

Once again, Ms. Strong and employees of the Analytical Laboratory Group, US Army Engineer Waterways Experiment Station were pleased to be hosts for the sixth annual Corps Chemist Meeting. The seventh annual meeting will be hosted by the Missouri River Division and personnel, with coordination by Ms. Strong. Tentative plans were made for the 1991 meeting to be held at the North Pacific Division.